

PATENT SPECIFICATION

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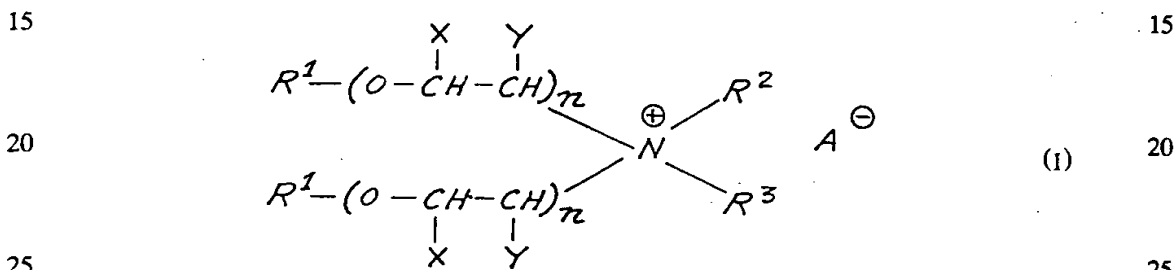
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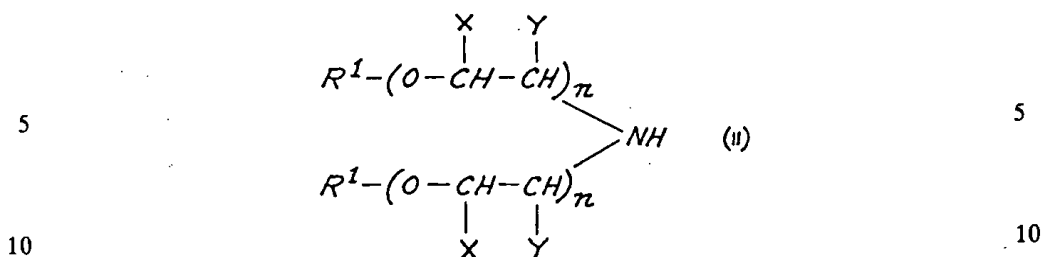
(54) QUATERNARY AMMONIUM COMPOUNDS, PROCESS FOR THEIR PREPARATION AND COMPOSITIONS CONTAINING THEM

- 5 (71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:
 10 This invention relates to quaternary ammonium compounds, to a process for preparing them and to hair care and fabric softening compositions containing them.
 The present invention provides quaternary ammonium compounds of the general formula



- 30 in which each R^1 is an alkyl or alkenyl group having from 8 to 30 carbon atoms, preferably from 14 to 24 carbon atoms, a cyclohexyl group or an aryl group which may be substituted by one or more alkyl groups, each X and Y is a hydrogen atom or a methyl group with the proviso that X and Y cannot both be methyl groups in the same alkyleneoxy group, each n is an integer from 1 to 20, preferably from 1 to 5, each of R^2 and R^3 is a benzyl group or an alkyl group having from 1 to 4 carbon atoms, preferably a methyl group, and A^\ominus is a methylsulfate, ethylsulfate, methylphosphate, bromide or, preferably, chloride ion.

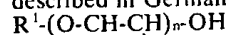
- 35 These compounds are prepared in accordance with the present invention by quaternization of one mole of secondary ether amine of the general formula



with one mole each of compounds of the formulae R^2A and R^3A , such as alkyl chloride or bromide, alkyl sulfate or benzyl chloride, in the presence of an alkali metal base.

The reaction is preferably carried out at an elevated temperature of from 30 to 160°C in a solvent, for example water, an alcohol, for example, ethanol or isopropanol, an aromatic hydrocarbon, such as toluene or xylene, or in a polar aprotic solvent, for example, dimethylformamide, and in the presence of an alkali metal base, such as sodium hydroxide, sodium carbonate or sodium bicarbonate; however, the reaction may be carried out at room temperature or without a solvent. In order to obtain uncoloured products, it is advantageous to carry out the reaction in the presence of an inert gas, for example, nitrogen.

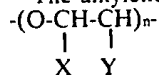
The secondary ether amines of the formula (II) can be obtained according to the process described in German Offenlegungsschrift 2555895 by reacting alkoxylates of the formula



in which R^1 , X, Y and n have the meanings given above, in the liquid phase with ammonia and hydrogen in the presence of a hydrogenation-dehydrogenation catalyst, especially a nickel or cobalt catalyst, at a gas rate of at least 10 l/kg of oxalkylate/h at a temperature of from 150 to 250°C and under a pressure of from 0.5 to 1.5 atmospheres gauge, and by eliminating the water of the reaction with the gas stream.

When R^1 is an alkyl or alkenyl group, the saturated and unsaturated alcohols upon which the alkoxy and alkenyloxy derivatives of the formula III are based and which form the group R^1 in the compounds of the formula I, may contain a primary, secondary or tertiary alcohol group. The alkyl or alkenyl group may be straight-chained or branched and is derived from a corresponding alcohol, for example, octyl alcohol, isononyl alcohol, lauryl alcohol, isotridecyl alcohol, isotridecyl alcohol, oleyl alcohol and stearyl alcohol. There may also be used mixtures of any two or more such alcohols, especially those which are formed by hydrogenation of natural fatty acids and/or their esters, for example, tallow fat alcohols, palm oil alcohols and coconut oil alcohols. Other alcohols from which the group R^1 may be derived are those which are obtained in industrial processes, for example, according to the Ziegler process (ethylene synthesis) which yields saturated primary alcohols having a straight carbon chain of up to 24 carbon atoms, and according to the various oxo processes which produce more or less branched alcohols. In addition, the group R^1 may be derived from aromatic hydroxy compounds, such as phenol, naphthols, 2,4,6-tri-tertiary butyl-phenol, 4-i-nonylphenol, 4-i-octylphenol, 4-i-propylphenol, cresol, xylenol and 4-i-dodecylphenol, or from cyclohexanol.

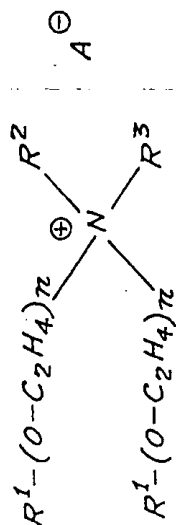
The alkyleneoxy group



is preferably derived from ethylene or propylene oxide and is introduced by reaction of the above alcohols and aromatic hydroxy compounds with ethylene- and/or propylene oxide. In this process there may also be used mixtures of ethylene oxide and propylene oxide, or the reaction may be effected first with ethylene oxide and then with propylene oxide.

The quaternary ammonium compounds of the present invention exhibit interesting surface-active properties which makes them suitable especially as components of hair care compositions. They are miscible with water and/or ethyl alcohol in all ratios. Those compounds having a higher degree of ethoxylation (about 10 to 20 units of ethylene oxide) yield clear solutions, whereas the compounds having a lower ethoxy content (up to 8 units of ethylene oxide) are easily dispersible to give turbid solutions. However, they are equally suitable as hair care compositions in either case.

Thus, liquid or pasty hair care compositions (so-called clear-rinse and cream-rinse compositions) with a good storage stability may be prepared simply by mixing the compounds with water. Any undesired excess of quaternary ether amine can be removed from the hair without



R ¹	n	R ²	R ³	AO	content of nitrogen showing an alkaline reaction in the starting compound
(C ₁₇ H ₃₅) ₂ -C ₆ H ₁₃	2	CH ₃	CH ₃	(CH ₃ O) ₂ SO ₃	1.79
"	4	CH ₃	CH ₃	"	1.54
"	8	CH ₃	CH ₃	"	1.16
n-C ₉ H ₁₉ -C ₆ H ₁₃	5	CH ₃	CH ₃	"	1.64
"	10	CH ₃	CH ₃	"	0.97
cyclohexyl	6	C ₂ H ₅	CH ₃	(C ₂ H ₅ O) ₂ SO ₃	1.72
C _{8/10} (43 % of C ₈ ; 55 % of C ₁₀)	2	CH ₃	C ₂ H ₅	(CH ₃ O) ₂ SO ₃	2.84
"	10	CH ₃	CH ₃	"	1.17
"	3	CH ₃	CH ₃	Cl	2.17
"	3	CH ₃	CH ₃	Cl	2.15
C ₁₂₋₁₄ (54 % of C ₁₂ ; 44 % of C ₁₄)	3	CH ₃	CH ₃	(CH ₃ O) ₂ SO ₃	2.13
C ₁₂₋₁₄ (33 % of C ₁₂ ; 64 % of C ₁₄)	3	CH ₃	CH ₃	"	1.53
isotridecyl	6	CH ₃	CH ₃	"	1.09
"	10	CH ₃	CH ₃	"	2.38
coconut oil alkyl	2	CH ₃	CH ₃	Cl	0.99
"	10	CH ₃	CH ₃	"	0.67
"	20	CH ₃	CH ₃	"	2.25
tallow fat alkyl	5	CH ₃	CH ₃	"	1.22
"	8	CH ₃	CH ₃	"	0.70
"	15	CH ₃	CH ₃	"	2.01
oleyl	2	CH ₃	CH ₃	"	1.12
"	8	CH ₃	CH ₃	"	0.97
"	10	CH ₃	CH ₃	"	0.85
"	12	CH ₃	CH ₃	Cl	0.66
"	15	CH ₃	CH ₃	Cl	

The basic-nitrogen content of the final product was 0 % in all cases, so that a complete quaternization had been reached.

- The following Table compares the foaming properties, measured according to the method of DIN 53 902, of the known compounds cetyltrimethyl ammonium chloride, cetyltrimethyl ammonium bromide and stearyl-pentaoxyethyl ammonium chloride with that of a quaternary etheramine compound according to the present invention, measured at 20 ° C after 25 strokes in a water of a hardness of 20° dH (German hardness) and a concentration of the active ingredient of 0.1 %.

- | | | |
|----|---|----|
| 10 | Cetyltrimethyl ammonium chloride, $C_{16}H_{33}N(CH_3)_3Cl$: 740 cm ³ | |
| | cetyltrimethyl ammonium bromide, $C_{16}H_{33}N(CH_3)_3Br$: | 10 |
| | stearyl-pentaoxyethyl ammonium chloride $C_{18}H_{37}(OCH_2CH_2)_5NH_3Cl$: 490 cm ³ | |
| | quaternary etheramine compound of the constitution: | |
| | di(dodecaoxyethylol-)-dimethyl ammonium chloride, | |
| 15 | $[C_{18}H_{35}(OCH_2CH_2)_{10}]_2N(CH_3)_2Cl$: 40 cm ³ | 15 |
- The following Application Examples illustrate various methods of using the quaternary etheramines for the preparation of cationic hair care compositions.

The quantitative data and the percentages in the following Examples are by weight.

EXAMPLE 8:

- | | | |
|----|---|----|
| 20 | Clear, hair-rinsing composition of low viscosity: | |
| | 1 % of di(pentadeca-oxyethylol-)-dimethyl ammonium chloride | 20 |
| | add 100 % of water | |

EXAMPLE 9:

- | | | |
|----|--|----|
| | Clear, liquid, hair-rinsing composition of high viscosity: | |
| | 1.5 % of di(deca-oxyethylol-)-dimethyl ammonium chloride | |
| 25 | 1.0 % of hydroxyethyl cellulose | 25 |
| | 0.3 % of perfume oil | |
| | ad 100 % of water | |

EXAMPLE 10:

- | | | |
|----|--|----|
| | Liquid, hair-setting lotion: | |
| 30 | 3.5 % of vinylpyrrolidone-vinylacetate copolymer in the ratio of 60:40 | 30 |
| | 0.2 % of di-isopropyl adipate | |
| | 0.3 % of perfume oil | |
| | 45 % of isopropyl alcohol | |
| | 0.2 % of di(pentadeca-oxyethylol-)-dimethyl-ammonium-methyl-sulfate | |
| 35 | ad 100 % of water | 35 |

EXAMPLE 11:

- | | | |
|----|---|----|
| | Hair lotion: | |
| | 0.2 % of di(dodeca-oxyethylol-)-dimethyl-ammonium-methyl -sulfate | |
| 30 | % of ethyl alcohol | |
| 40 | 0.4 % of di-isopropyl adipate | 40 |
| | 0.2 % of perfume oil | |
| | ad 100 % of water | |

EXAMPLE 12:

- | | | |
|----|--|----|
| | Shampoo: | |
| 45 | 1.4 % of di(deca-oxyethylol-)-dimethyl-ammonium -ethyl-sulfate | 45 |
| 15 | % of lauryldiglycol-ethersulfate-sodium salt | |
| | 3 % of coconut oil acid-diethanolamide | |
| | 0.3 % of perfume oil | |
| | 1.2 % of sodium chloride | |
| 50 | 0.1 % of formalin | 50 |
| | ad 100 % of water | |

EXAMPLE 13:

- | | | |
|----|---|----|
| | Hair-rinsing composition in emulsion form: | |
| 55 | 2 % of di(pentadeca-oxyethylstearyl) -dimethyl-ammonium-methyl -sulfate | 55 |
| | 3 % of stearyl alcohol + 10 moles of ethylene oxide | |
| | 2 % of triethylene-glycol-distearate | |
| | 3 % of cetyl alcohol | |
| | 0.1 % of perfume oil | |
| | ad 100 % of water | |

EXAMPLE 14:

Hair-rinsing composition in cream form:

0.5 % of distearyl-dimethyl-ammonium chloride

5 1 % of di(dodecaoxyethylolyl)-dimethyl-ammonium chloride

3 % of cetyl/stearyl alcohol + 9 moles of ethylene oxide

4 % of cetyl alcohol

0.2 % of perfume oil

ad 100 % of water

EXAMPLE 15:

10 Hairdressing cream:

0.2 % of di(decaoxyethylolyl)-dimethyl -ammonium chloride

5 % of diglycerol sesquileate

15 % of paraffin wax

1 % of silicone oil

15 15 % of Vaseline (registered Trade Mark)

2 % of paraffin oil

0.1 % of perfume oil

ad 100 % of water

EXAMPLE 16:

20 Hair spray:

1.5 % of polyvinylpyrrolidone/vinylacetate copolymer, ratio of 70:30

0.1 % of perfume oil

0.1 % of silicone oil

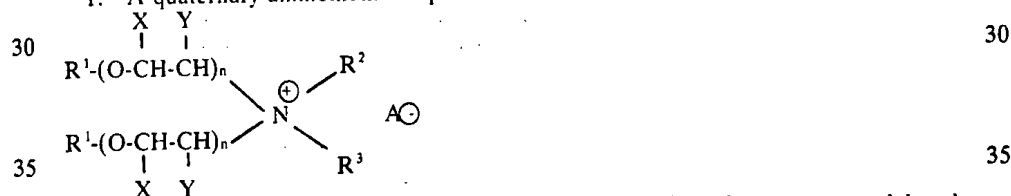
0.2 % of di(pentadecaoxyethylolyl)-dimethyl-ammonium chloride

25 28 % of ethyl alcohol

ad 100 % of fluorinated hydrocarbons as propellent gas.

WHAT WE CLAIM IS:

1. A quaternary ammonium compound of the formula



in which each R¹ is an alkyl or alkenyl group having from 8 to 24 carbon atoms, a cyclohexyl group or an aryl group which may be substituted by one or more alkyl groups, each X and Y is a hydrogen atom or a methyl group with the proviso that X and Y cannot both be methyl groups in the same alkyleneoxy group, each n is an integer from 1 to 20, each of R² and R³ is an alkyl group having from 1 to 4 carbon atoms or a benzyl group, and A⁻ is a methylsulfate, ethylsulfate, methylphosphate, chloride or bromide ion.

2. A compound as claimed in claim 1, in which X and Y are both hydrogen atoms.

3. A compound as claimed in claim 1 or claim 2, in which R² and R³ is a methyl or ethyl group.

4. A process for the preparation of a quaternary ammonium compound as claimed in claim 1, which comprises reacting one mole of a secondary etheramine of the formula



in which R¹, X, Y and n have the meanings specified in claim 1, with one mole each of compounds of the formula R²A and R³A in which R², R³ and A have the meanings specified in claim 1, in the presence of an alkali metal base.

5. A process as claimed in claim 4, wherein the reaction is carried out in a solvent.

60 6. A process as claimed in claim 4 carried out substantially as described in any one of Examples 1 to 7 herein.

7. A quaternary ammonium compound as claimed in claim 1 whenever prepared by a process as claimed in any one of claims 4 to 6.

8. A hair care or fabric softening composition comprising an aqueous and/or alcoholic

solution or dispersion of one or more quaternary ammonium compounds as claimed in claim 1.

9. A hair care composition substantially as described in any one of Examples 8 to 16 herein.

5 10. A fabric softening composition comprising from 1 to 15 % by weight of one or more compounds as claimed in claim 1 in aqueous solution or dispersion. 5

11. A fabric softening composition comprising from 20 to 35% by weight of one or more compounds as claimed in claim 1 in aqueous solution or dispersion.

10 12. A method for treating the hair, which comprises applying thereto a hair care composition as claimed in claim 8 or claim 9. 10

13. A method for softening a textile fabric, which comprises applying thereto a fabric softening composition as claimed in claim 8 or claim 10.

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